

THE CATALYTIC ACTIVITY OF CHROMITES FOR
THE OXIDATION OF CARBON MONOXIDE

BY
EARL CHRISTIAN LORY

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS
HOPKINS UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
1932

BALTIMORE
THE WILLIAMS & WILKINS COMPANY
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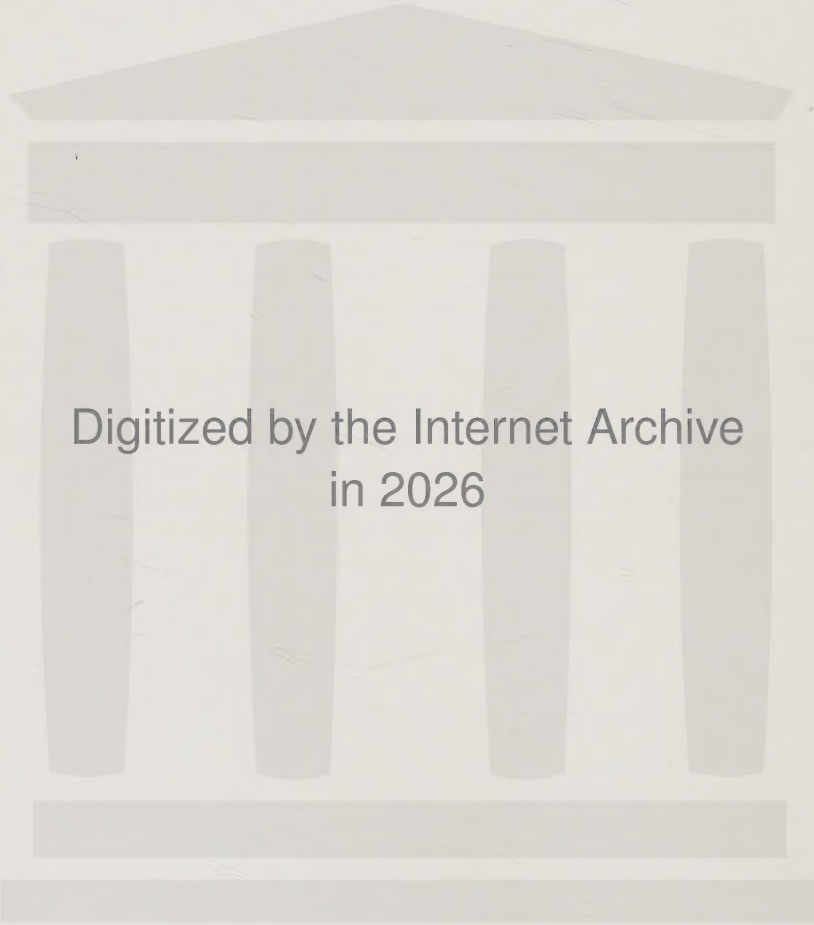
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THE CATALYTIC ACTIVITY OF CHROMITES FOR THE OXIDATION OF CARBON MONOXIDE¹

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The metal oxide and mixed metal oxide catalysts for the oxidation of carbon monoxide have received considerable attention since the investigations of Lamb, Bray, and Frazer (1). Bone (2) and his coworkers studied the oxidation of carbon monoxide using nickel, copper, and their oxides. Bennett (3) studied the activity of a number of purified oxides and found manganese, nickel, and cobalt oxides to be especially active at low temperatures. Recently Engelder and Miller (4) have shown that a mixed catalyst of titania and copper oxide was active, and Engelder and Blummer (5) have shown that a catalyst composed of cobaltic and ferric oxides has a high degree of activity in a temperature range of 0°C. to 200°C. Frazer (6) has shown that a catalyst composed of ferrous chromite is active at elevated temperatures.

This paper records the results of a continuation of work upon metal chromites as catalysts for the high temperature oxidation of carbon monoxide.

EXPERIMENTAL PART

Preparation of catalysts

The chromites were prepared by two methods, the method of Gerber (7) and the method of Lazier (8). The method of Gerber is as follows: A mole of the anhydrous metal chloride was ground with a mole of potassium dichromate to a fine powder. The mixture was fused in a porcelain dish at 900°C. for one hour. The resulting mass was leached with boiling water and concentrated hydrochloric acid, and then dried. It was found impossible to prepare cupric chromite by this method, as at 900°C. the cupric chromite decomposed forming cuprous chromite, which gradually reoxidized to cupric chromite upon cooling and yielded a mixture of cupric chromite and chromium oxide.

¹ The material in this communication is abstracted from the dissertation submitted by E. C. Lory in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Johns Hopkins University, June, 1932.

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The method of Lazier consists of the preparation of a "metal ammonium chromate" and its subsequent decomposition, forming a mixture of the metal chromite and the metal oxide. The preparation of cobaltous chromite is given as an example. One mole of cobalt nitrate dissolved in 300 cc. of water was mixed with one mole of chromic trioxide in 100 cc. of water. The resulting solution was heated to 80°C. and to it was added three moles of ammonia. The resulting dark red precipitate was filtered by suction and washed sparingly with water and dried at 110°C. The dried precipitate was decomposed by heating small quantities in a casserole over a free flame. This gave an extremely fine greenish black powder composed of an equimolar mixture of cobalt oxide and cobaltous chromite. This was leached with concentrated hydrochloric acid until the acid gave no reaction for cobalt. The resulting chromite was a fine dark green powder.

Catalytic activity of chromites

The method used in testing the catalytic activity of the chromites for the oxidation of carbon monoxide consisted in the direct comparison between the catalyst and a catalyst known to be 100 per cent efficient. The apparatus and method developed by Bennett (3) was used with slight modifications. The dried gas mixture containing 1 per cent carbon monoxide was passed over the catalyst at the rate of 100 cc. per minute. The catalyst bed was 1 sq. cm. in area and 10 cm. deep. It was contained in a glass tube so arranged that the gases were preheated before passing over the catalyst. The carbon dioxide formed was removed by passing the gas through standard barium hydroxide. The remaining gases were dried and passed over hopcalite. This quantitatively oxidized any remaining carbon monoxide, the carbon dioxide formed being absorbed in a second absorption flask. The excess barium hydroxide in the two absorption flasks was titrated with standard oxalic acid. A direct comparison of the barium carbonate present in the two flasks gave the efficiency of the catalyst and was not affected by fluctuations in the rate of flow or concentration of carbon monoxide in the testing gas. With this method good checks were obtained with a similar catalyst at identical temperatures.

Table 1 gives the results of the tests upon the various chromites, giving the temperatures at which they possess 10, 20, 40, 60, 80, 90, and 100 per cent efficiency in the oxidation of a 1 per cent carbon monoxide-air mixture.

Surface oxidation of chromites

It has been noticed by O. G. Bennett that upon heating a chromite and washing with water, the filtrate was slightly colored. It was thought that this coloration might be due to the chromic acid formed by the oxidation of the chromite during heating. Tests were made upon copper, cobalt,

and nickel chromites to determine if oxidation did occur and the extent of oxidation.

Experimental procedure. A 10-g. sample of the chromite was weighed into a Gooch crucible and leached with hot water until no test for chromic acid could be obtained in the filtrate. The crucible was then heated in an electric furnace to the desired temperature. It was leached with hot water in 200-cc. portions. The amount of chromic acid was determined iodometrically by titration with 0.01 *N* sodium thiosulfate. In most cases three to five leachings were required to remove completely the chromate present. The results of the surface oxidation on copper, cobalt, and nickel chromites are given in table 2, showing the temperature and time (in hours) of heating, with the per cent of CrO_3 by weight obtained in the filtrate.

These results tend to show that upon the heating of a chromite the surface of the chromite is oxidized to a chromate, but that the oxidation is only on the surface. To determine whether or not it was a case of equilibrium, a sample of copper chromite No. 3 was heated in a steel bomb at 400°C. under a pressure of 55 atmospheres of oxygen for twenty-four hours. Upon being leached it showed the same amount of chromate as when it was heated at atmospheric pressure.

Reduction of surface chromate by carbon monoxide

If the formation of chromate on the surface of a chromite is the active agent in the oxidation of carbon monoxide, the reduction of the chromate must occur at, or below, temperatures at which the chromite is catalytically active. Tests were carried out upon copper and cobalt chromites to determine whether or not the chromate present on the surface of the chromite was reduced by carbon monoxide.

The method of determining the reduction by carbon monoxide was to pass carbon monoxide over the chromite and absorb the carbon dioxide formed in standard barium hydroxide. Nitrogen was used to give an oxygen-free atmosphere.

Copper chromite No. 3. Reduction of the chromate and also of the copper oxide present took place at 100°C. The amount of carbon dioxide was in considerable excess of the amount of chromate present due to the simultaneous reduction of the copper oxide. Upon leaching after reduction no chromate was found to be present.

Cobalt chromite No. 1. Cobalt chromite was studied in more detail, as the cobalt oxide was not reduced by the carbon monoxide and quantitative checks of the amount of chromate present could be obtained. Reduction was observed when the temperature of the chromite reached approximately 160°C. Upon leaching with hot water a small amount of chromate was found to remain and not be reduced by the carbon monoxide at 200°C.

TABLE 1

Efficiency of catalysts used in the oxidation of a carbon monoxide-air mixture

CATALYST	TEMPERATURES (°C.) AT WHICH CATALYST HAS EFFICIENCY OF						
	10 per cent	20 per cent	40 per cent	60 per cent	80 per cent	90 per cent	100 per cent
Copper chromite*							
No. 1.....	30	31	33	35	46	61	94
No. 2.....	103	125	152	168	178	183	199
No. 3.....	44	57	74	91	118	120	142
No. 4.....	107	116	129	140	149	153	165
No. 5.....	55	78	82	84	85	87	102
Copper dichromate†							
No. 1.....	106	129	153	170	194	217	265
No. 2.....	217	239	273	300	327	341	357
Cobalt chromite‡							
No. 1.....	230	255	283	300	323	349	386
No. 2.....	66	84	100	100	101	104	111
No. 3.....	147	169	196	210	222	229	243
Ferrous chromite§							
No. 1.....	136	154	182	199	218	231	254
No. 2.....	216	239	248	270	304	400	—
Nickel chromite¶							
No. 1.....	259	283	320	353	383	398	431
Manganous chromite							
No. 1.....	235	259	285	298	313	341	420

* Copper chromite:

- No. 1. Copper chromite prepared from "copper ammonium chromate," decomposed but not leached.
- No. 2. Copper chromite from "copper ammonium chromate," leached with concentrated hydrochloric acid.
- No. 3. Copper chromite from "copper ammonium chromate," leached with concentrated hydrochloric acid and heated to 700°C.
- No. 4. Copper chromite No. 3 heated in a bomb for twenty-four hours at 400°C. under a pressure of 55 atmospheres of oxygen in the hope of increasing the oxidation of the chromite to chromate.
- No. 5. Catalyst prepared by precipitation of cupric carbonate upon a sample of copper chromite No. 3. Heated to 170°C. for three hours with the carbon monoxide mixture passing over it, and then tested. No. 1 and No. 5 have nearly identical activities.

† Copper dichromate:

- No. 1. Copper dichromate prepared by saturating a solution of chromic acid with basic copper carbonate and slowly evaporating at room temperature in a vacuum. Material heated to 250°C., cooled, and tested.
- No. 2. Cupric dichromate, Eimer and Amend c. p. crystalline material, heated for eight hours at 150°C. and at 215°C. for six hours. Upon completion of testing, a Bunsen active oxygen test showed the presence of 76 per cent cupric dichromate.

‡ Cobalt chromite:

No. 1. Cobalt chromite prepared by Gerber's synthesis.

No. 2. Decomposition product of "cobalt ammonium chromate." Not leached.

No. 3. Cobalt chromite from "cobalt ammonium chromate," leached with concentrated hydrochloric acid until free of cobaltous oxide.

§ Ferrous chromite:

No. 1. Decomposition product of "ferric ammonium chromate." Not leached.

No. 2. Ferrous chromite prepared by Gerber's synthesis.

¶ Nickel chromite:

No. 1. Nickel chromite prepared by Gerber's synthesis.

|| Manganous chromite:

No. 1. Manganous chromite prepared by Gerber's synthesis.

TABLE 2

Surface oxidation on copper, cobalt, and nickel chromites

TEMPERATURE	TIME	PER CENT CrO_3	TEMPERATURE	TIME	PER CENT CrO_3
Copper chromite No. 3					
Test No. 1			Test No. 2		
<i>degrees C.</i>	<i>hours</i>		<i>degrees C.</i>	<i>hours</i>	
200	10	0.0504	130	36	0.0100
450	1	0.0663	160	73	0.0212
330	10	0.0660	450	2	0.0651
300	2	0.0641	300	3	0.0663
300	16	0.0688	328	7	0.0693
100	250	0.0001	300	8	0.0664
Average for high values = 0.0678 per cent CrO_3					
Cobalt chromite No. 1					
Test No. 1			Test No. 2		
450	6	0.0728	300	18	0.0680
300	6	0.0623	500	5	0.0728
300	11	0.0720	530	5	0.0734
200	12	0.0332	900	6	0.0730
500	7	0.0730	160	1168	0.0102
Average for high values = 0.0738 per cent CrO_3					
Nickel chromite No. 1					
Test No. 1			Test No. 2		
430	5	0.0251	500	11	0.0256
460	5	0.0252	500	3	0.0240
410	3	0.0262	675	3	0.0241
400	84	0.0276	500	12	0.0236
530	73	0.0244	500	10	0.0262
800	3	0.0261	800	3	0.0253
Average for high values = 0.0260 per cent CrO_3					

The results of the reduction of cobalt chromite are given in table 3, giving the number of cubic centimeters of 0.01 *N* thiosulfate solution required to titrate the chromate present.

TABLE 3
Results of the reduction of cobalt chromite

TEST NO. 1		TEST NO. 2	
Chromate by leaching	22.61 cc.	Chromate by leaching	22.05 cc.
Chromate by reduction	23.33 cc.	Chromate by reduction	21.79 cc.
Chromate by reduction	22.81 cc.	Chromate by reduction	19.41 cc.

These results indicate that the chromate formed upon the surface of the chromite is reduced by carbon monoxide at the same temperatures at which the chromites become catalytically active.

Adsorption of DuPont Scarlet 2RL by chromites

Paneth and Vorwerk (9) have shown that Ponceau 2R is adsorbed on the surface of crystalline lead sulfate apparently in a monomolecular layer, and by adsorbing it on a surface of known area they have calculated the area occupied by one molecule of the dye when it is adsorbed upon the surface of lead sulfate. The adsorption of the dye upon copper, cobalt, and nickel chromites has been measured. In these experiments DuPont Scarlet 2RL was used; as it is the same dye chemically as Ponceau 2R.

TABLE 4
Adsorption of DuPont Scarlet 2RL upon chromites

CHROMITE	WEIGHT OF DYE ADSORBED BY 1 GRAM OF CHROMITE $\times 10^4$ GRAMS	MOLES OF DYE ADSORBED BY 1 GRAM OF CHROMITE $\times 10^7$	NUMBER OF MOLECULES OF DYE ADSORBED $\times 10^{-17}$	SPECIFIC SURFACE OF CHROMITES $\times 10^{-3}$ SQ. CM.
CuCr ₂ O ₄	5.71	11.89	7.21	14.38
CoCr ₂ O ₄	9.63	20.05	12.15	24.23
NiCr ₂ O ₄	2.20	4.58	2.78	5.54

The method used was that of Paneth and Vorwerk. One and one-half grams of chromite was weighed into an ampoule of about 15 cc. capacity. Ten cubic centimeters of the dye solution was admitted with a pipette, the ampoule sealed, shaken for an hour and then centrifuged. Ten solutions of increasing concentration were used to obtain an adsorption isotherm at room temperature. Five cubic centimeters of the clear supernatant liquid was pipetted out and diluted to a dilution easily read upon the colorimeter. The comparison was made by means of a Bausch and

Lomb colorimeter. The results of the adsorptions of DuPont Scarlet 2RL upon the chromite are shown in table 4.

Owing to the high concentration of dye necessary to reach saturation of the surface and the attendant difficulties in determining the amount adsorbed, the results given in table 4 are not accurate to better than 10 per cent.

Combining the amount of surface found by dye adsorption with the amount of chromic acid found by leaching, the area occupied by each chromium atom can be calculated. The results are shown below.

	<i>Area occupied by each chromium atom on the surface</i>
Cobalt chromite.....	5.49×10^{-15} sq. cm.
Nickel chromite.....	3.52×10^{-15} sq. cm.
Copper chromite.....	3.50×10^{-15} sq. cm.

X-ray diffraction patterns were taken of cobalt, copper, and nickel chromites to determine whether or not the chromites prepared in this investigation were true chromites or mixtures of the oxides. Powder diagrams showed them to be definite compounds and not mixtures. Copper chromite was apparently not a cubic lattice and the x-ray investigation of this compound is being continued.

DISCUSSION

There are two possible explanations for the activity of the chromites in the oxidation of carbon monoxide: (1) the adsorption of the carbon monoxide with its activation through adsorption, or (2) the adsorption and activation of the oxygen. From the results of the surface oxidation of the chromites and the reduction of the chromate formed it would seem more logical that the activity is due to the adsorption of oxygen to form a chromate and its activation through a chemical formation. The activation of the saturated oxygen molecule would seem to be the more important factor, rather than the activation of the unsaturated carbon monoxide molecule.

The activity of the decomposition product of the "metal ammonium chromate" appears to be due to the presence of the metal oxide. When this mixture is leached with acid the oxide is removed, and the activity is then due to that of the chromite.

The oxidation of the chromites to chromate seems to be limited to a surface reaction, as increased heating under high pressure of oxygen did not increase the amount of chromate formed. The chromate appears to form a surface film that prevents further oxidation.

Studies of the adsorption of carbon monoxide, oxygen, and carbon dioxide by the chromite and chromate surfaces are now being carried out.

SUMMARY

1. The catalytic activity of copper, cobalt, nickel, manganous, and ferrous chromites for the oxidation of carbon monoxide has been determined.

2. It has been shown that upon heating the chromites are oxidized to sexivalent chromium on the surface, the surface film preventing further oxidation.

3. The chromate formed on the surface of the chromite is reduced by carbon monoxide at, or below, the temperatures of catalytic activity of the chromite for oxidation of carbon monoxide.

4. The specific surface of the chromites was determined by the method of Paneth and Vorwerk through adsorption of DuPont Scarlet 2RL.

5. An explanation of the activity of the chromites for the oxidation of carbon monoxide through the formation of a surface compound has been proposed.

The writer wishes to express here his appreciation to Professor J. C. W. Frazer, at whose suggestion and under whose supervision the work described was carried out.

He also wishes to thank Dr. O. G. Bennett for supplying him with a sample of ferrous chromite and for his helpful criticism during this investigation.

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BIOGRAPHY

Earl Christian Lory was born near Windsor, Colorado on June 25, 1906. He received his elementary education in the schools of Fort Collins, Colorado. He entered the Colorado Agricultural College in 1924 and received the B.S. Degree in Chemistry in 1928.

He entered the Faculty of Philosophy of the Johns Hopkins University as a graduate student in the Chemistry Department in the fall of 1928.

During the session of 1931-32 he was the Harry Clary Jones Fellow.

